D.1 - Technologies for (in situ) remediation and management of soil contamination

POTENTIAL OF A COMBINED TECHNIQUE OF ULTRASOUND WAVES AND ADDITIVES TO ENHANCE THE *EX SITU* SOIL WASHING PROCESS.

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Introduction

The *ex situ* physico-chemical treatment of soils by soil washing is an often used method to remediate soils contaminated with organic and/or inorganic compounds. During the washing process, the contaminated soil is divided into different fractions of fine sand and gravel which can be used as secondary raw material. Because contaminants bind strongly to the clay and loam particles and the organic material in the soil, a rest fraction of silt and organic material remains after the washing process. These fractions are highly contaminated and are not allowed to be reused. With the best available techniques, it is not profitable to clean these fractions, so they can only be disposed or burned at high costs. In addition, heavy contaminated soils with too many organic matter or clay are insufficiently cleaned in the soil wash installation. Therefore soil washing centers are forced to refuse soils which do not meet the criteria and are interested in new technologies to upgrade their systems in order to meet their limitations.

This study proposes the combined use of ultrasound waves and additives to enhance the washing process of the soil. Scientific research shows that high frequency sound waves (> 20 kHz) cause strong mechanic distortions and 'hot spots' of high temperatures and pressures in a liquid. These effects originate from the strong implosions of gas bubbles which arise in the liquid and grow to a critical volume (Figure 1A). When the implosion occurs nearby a surface, as shown in Figure 1B, high-jet streams are formed which impact on the surface at high speed (400 km/h) (Suslick, 1989). The impact of these streams is so powerful that the surface becomes damaged (Kaiser et al. 2012) (Figure 1C) . The mechanical streaming and violent collapse of the microbubbles cause shearing, shock waves and local jet streams towards particles. These effects result in intensive mixing, the partial destruction of particles and distortion of the stagnant water layer, thereby enhancing the leaching process of the compounds from the particles (Mason et al. 2004, Shrestha et al. 2009, Swamy and Narayana 2006). Leaching using ultrasound waves results in higher removal efficiency with shorter process time compared to mechanically stirring (Son et al. 2011). Different authors published the release of different types of organic contaminants from the soil due to ultrasound such as chlorinated aromatic compounds (Beard et al. 1992, Shrestha et al. 2009), polyaromatic hydrocarbons (Shrestha et al. 2009, Duong et al. 2010) and petroleum hydrocarbons (Son et al. 2011). The degree of enhancement varies with many factors, such as soil type, soil/water ratio, temperature, wave frequency and energy input (Kim and Wang 2003, Feng and Aldrich 2000). The addition of solubilizing agents, such as surfactants, can enhance this process even more by complexating the released contaminants and keeping them in solution. Mulligan et al. (2001) gave a review of different biosurfactants and their potential to remediate contaminated soils.

Beside the physical effects, ultrasound waves can contribute to the chemical degradation of mineral oil due to the decomposition of water into the highly reactive hydroxyl radicals (Weiss 1944) and the strong oxidant, hydrogen peroxide (Fitzgerald et al. 1956). Sonication could, therefore, not only enhance the leaching process, but also completely destroy the contaminants. However, the production of these oxidative compounds is rather limited and by adding oxidizing agents, such as H_2O_2, this process can be further improved (Gogate, 2008; Lin et al., 1996).

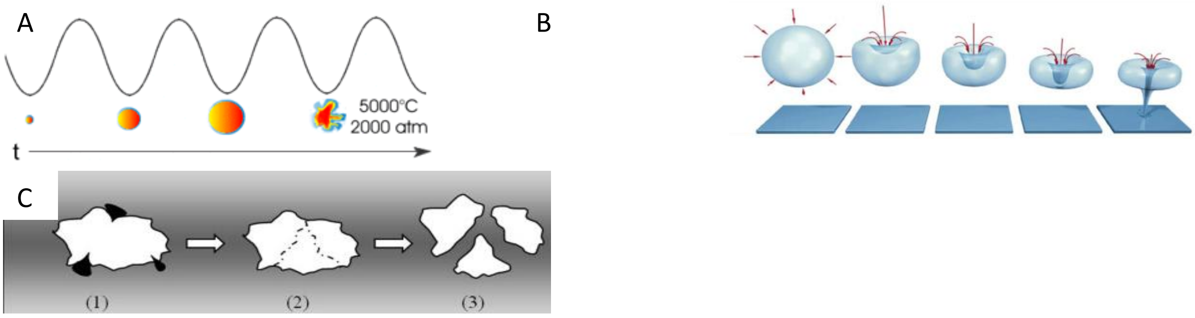

Figure 1: Overview of the effects resulting from ultrasound waves in a liquid: (A) subsequently growth and implosion of microbubbles, (B) the formation of a jet stream by the implosion of cavitation bubbles near a surface (FOCUS-IT, LLC.) and (C) the effect of jet streams on a soil particle (Bendicho et al. 2012).

The integration of this technique in soil wash installations would improve the best available techniques to clean soils physico-chemically (Thangavadivel et al. 2011). However, despite promising publications, the overall research regarding this technology to enhance the remediation of organic contaminated soil is rather limited. Therefore, the current study investigates the potential of a combined technique of ultrasound waves (US) and oxidizing additives and/or solubilizing additives. The aim of this study is to test whether significant larger amounts of mineral oil can be removed from contaminated soils by using the combination of US and additives in order to determine its potential to improve the current industrial soil washing process.

Materials and Methods

Experiments were performed with a soil contaminated with 2175.5 (±7.6%) mg mineral oil/kg dry weight. A soil slurry of 250 mL was treated with the ultrasonic processor UP200S (Hielsher) equipped with a S14 probe Hielscher (24 kHz) as shown in Figure 2. During treatment, the solution was cooled in an ice bath to maintain room temperature. To compare the type of mixing, a distinction was made between mechanical mixing and US.

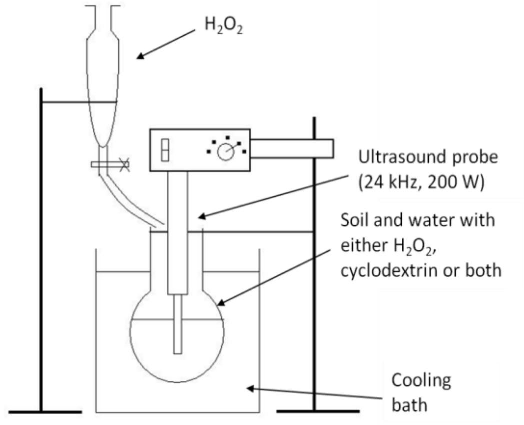

Figure 2: Experimental set-up of the ultrasound-assisted leaching process.

Conditions, such as type of additive (H_2O_2, cyclodextrin and the combination), treatment time (3 or 2 h), energy input (200 or 100W) and liquid/solid ratio (10 or 5) were varied. The type of cyclodextrin was randomly-methylated-β-cyclodextrin, obtained from Wacker Chemie. Cyclodextrin (5 g/L) was added from the beginning of the treatment, while H_2O_2 (10 mol/L) was continuously added to the soil slurry at a rate of approximately 1 mL/min during treatment until a final concentration of 5 M was obtained in a final volume of 250 mL.

An overview of the test conditions is given in Table 1. As a reference, a treatment with mechanical stirring (400 rpm) or US, but without additives was performed. All experiments were performed singly as a screening test. A 7.6% variation in the concentration of mineral oil in the soil occurred due to analysis.

Table 1: Overview of the test conditions. Each condition was tested with either mechanically stirring or ultrasound waves.

Condition tested	L:S (mL/g)	Time (min)	Type of Additive	Concentration of additive	Energy US
Reference test	10	180	None	/	200W
Type of additive	10	180	Cyclodextrin	5 g/L	200W
	10	180	H_2O_2	5 M	200W
	10	180	H_2O_2 Cyclodextrin	5 M 5 g/L	200W
Treatment time	10	120	H_2O_2	5 M	200W
Energy input	10	180	H_2O_2	5 M	100W
L:S ratio	5	180	H_2O_2	5 M	200W

After the treatment, soil and water were separated by filtering. The amount of mineral oil remaining in the soil was determined by accelerated solvent extraction, an extraction procedure at high temperature (100°C) and pressure (70 bar) using 50% acetone and 50% n-hexane as extraction solvents. The mineral oil in the extract was quantified using a GC-FID (Agilent) equipped with a DB-5ms column (30 m x 0.25 mm, 0.25 µm). Volumes of 1 µL were injected on the column with helium as carrier gas. The inlet temperature was set at 270 °C. The initial temperature of the column was maintained at 50 °C for 3 min after which the temperature increased with 25 °C/min until 315 °C was obtained. After 20 min, the temperature decreased again until 50 °C. The temperature of the detector was set at 300°C. A surface sum between C10 and C40 was used to calculate the concentration of mineral oil in the sample. The concentration of mineral oil was calculated based on a calibration curve made with a standard mineral oil solution from the Dutch Institute of Public Health and the Environment (RIVM). The amount of mineral oil removed was calculated based on the initial concentration.

Results

Effect of ultrasound waves

The leaching tests with stirring and US without additives gave the same removal of 23% and 24%, respectively. As such, US alone did not significantly enhance the removal of mineral oil. This is in contrast with previous publications in which an enhanced leaching was observed with 40% - 90 % removal depending on the treatment time, power, soil/liquid ratio (Feng and Aldrich 2000, Kim and Wang 2003, Son et al. 2011) . However, these experiments were always performed with soils freshly spiked with mineral oil (diesel), while the current study was performed with aged contaminated soils. In addition, Son et al. (2011) observed that the combination of mechanically mixing and ultrasound waves to achieve both macro and micro mixing is necessary to maximize the leaching process. Finally, Feng and Aldrich (2000) hypothesized that at prolonged sonication time, re-adsorption occurs, which already occurred after 5 min of sonication time. Other authors, observed a maximum desorption between 5 min – 60 min (Mason et al. 2004).

Effect of additives with mechanical stirring

From the additives, H_2O_2 during stirring resulted in the highest removal% (68%), while 5 g/L cyclodextrin did not remove significant more mineral oil from the soil than stirring without cyclodextrin. In contrast, it appeared that less mineral oil dissolved in the water. Other experiments with cyclodextrins, however, showed a significant higher solubility of mineral oil in presence of 5 g/L cyclodextrin concentration although this was at a much lower liquid solid ratio (1/3) (own data, unpublished). The reason for this remains unclear.
Combining both additives did not significantly enhance the removal efficiency. In addition to the low contribution of cyclodextrin to dissolve mineral oil in the current experiment, cyclodextrin might have been oxidized during the process, however additional experiments showed no significant degradation of cyclodextrin by H_2O_2 alone.

Effect of additives in combination with ultrasound waves

With ultrasound, cyclodextrin removed significant more mineral oil (43.9 %) from the soil than in absence of ultrasound (15.8 %). So it seems that the uptake of mineral oil by the solubilizing agent enhanced with US.
In contrast, the combination ultrasound/H_2O_2 only decreased the mineral oil with 53%, which is not significantly higher than without ultrasound. Degradation of the mineral oil can occur by H_2O_2 itself, the hydroxyl radicals produced by both ultrasound and the decomposition of H_2O_2 or a combination. However, ultrasound might also accelerate the decomposition of H_2O_2 into H_2O and O_2. An increased gas production was indeed observed in the presence of ultrasound. In addition, the formed hydroxyl radicals might be scavenged by the excess of H_2O_2 (Gogate et al. 2008). For these reasons, a part of the H_2O_2 was not used for the degradation of mineral oil. Although the amount of hydroxyl radicals was not monitored, we hypothesize from the observations that the net amount of hydroxyl radicals was insufficient to enhance the removal of mineral oil. This is in contrast to previous reports where an enhanced degradation was observed (Lin et al. 1996, Suri et al. 2008, Visscher and Langenhove, 1998). However, because of the different parameters such as type of contaminant, reaction time,

frequency and/or concentration of H_2O_2 it is difficult to compare the results. In addition, these experiments were performed with artificial contaminated water and not in soil slurries. For example, Suri et al. (2008) observed that 70% more 2-chlorophenol was degraded when US/H_2O_2 was used, compared to H_2O_2 alone. However, this was observed at a relative high H_2O_2/COD dosage and a significant lower reaction time (60 min).

When using a combination of oxidizing and complexating additives in the presence of an acoustic field, the removal efficiency decreased considerably. Probably, a large part of the hydroxyl radicals originating from H_2O_2 and/or US were lost by the degradation of the cyclodextrins and therefore not available for the degradation of mineral oil. Monitoring the cyclodextrin concentration during the different treatments indeed indicate the partially destruction of cyclodextrin in presence of US/H_2O_2 (data not shown). However, the analysis was insufficient to determine whether or not the ring was destroyed.

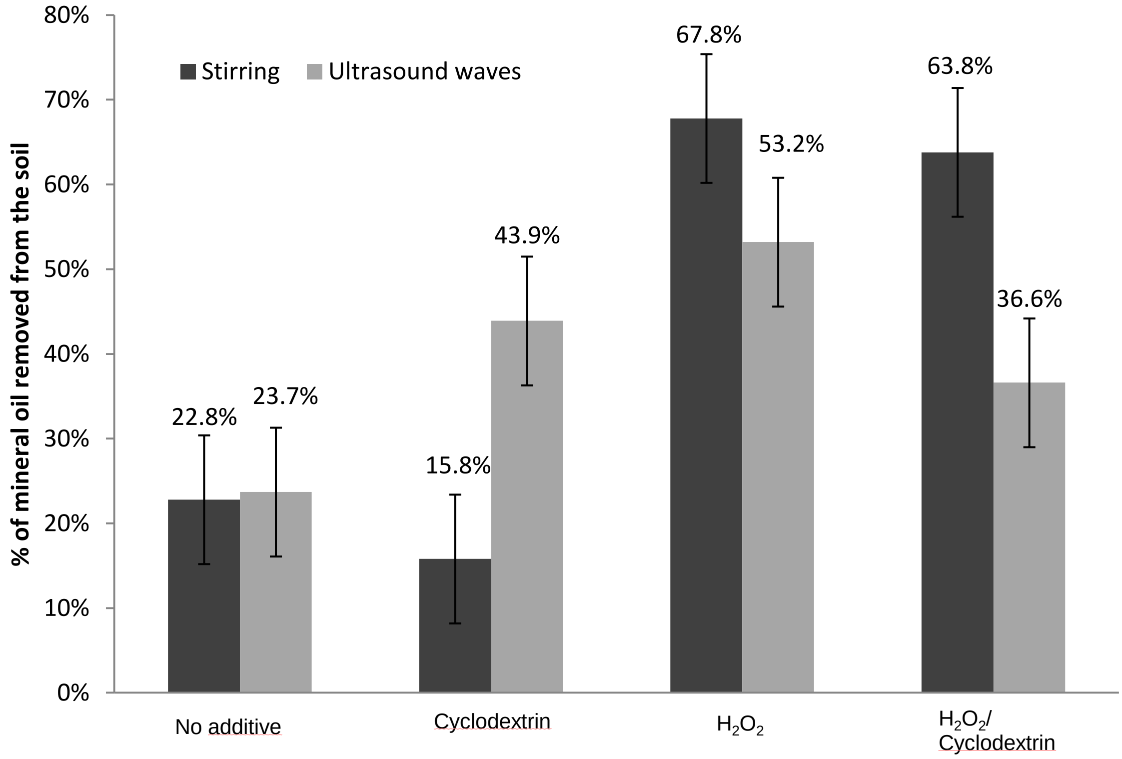

Figure 2: Percentage of mineral oil removed from the soil using different additives combined with mechanically stirring or ultrasound waves. Error bars are 7.6%, which is the average variation of the initial mineral oil concentration in the soil.

Effect of different process parameters on the removal efficiency of H_2O_2 and US/H_2O_2

By decreasing the reaction time with H_2O_2 to 2 h during stirring, 11 % less mineral oil is removed from the soil, while with US, there is as much mineral oil removed. Also, when using ultrasound waves there is no negative effect when the energy input decreases to 100 W or when the amount of soil in the liquid doubles. In contrast, when a soil slurry with a lower L:S ratio is mixed, 13% less mineral oil is removed from the soil. These results indicate that a technique using oxidative additives in combination with acoustic energy to enhance the removal process can become more interesting when the reaction time, power and L:S ratio are optimized as energy requirements can be reduced.

Conclusion

These preliminary experiments demonstrate that the use of US/cyclodextrin and stirring/H_2O_2 significantly enhances the removal of mineral oil from the soil and has a high potential in improving the current industrial soil washing process. The technology could be applied as pretreatment to release the contaminants more easily from the soil in order to achieve more amounts of the reusable fraction with higher purity. Rest fractions, on the other hand, could be subjected to similar treatment to lower the contaminant concentration in order to reuse them as secondary raw material. However, more research is necessary to optimize the conditions (reaction time, ultrasound power and L:S ratio) to obtain a technical and economical interesting new soil washing process.

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